PLASMA MODIFICATION OF Si-O-Si BOND STRUCTURE IN POROUS SiCOH FILMS

F. N. Dultsev [1], A. M. Urbanowicz [2,3] and M. R. Baklanov [2],
[1]Institute of Semiconductor Physics SB RAS, Novosibisrk, 630090, Lavrentiev ave., 13, Russia
[2]IMEC, Leuven, Belgium
[3] Department of Chemistry, Katholieke Universiteit Leuven, Belgium

ABSTRACT

Plasma modification of SiOCH low-k films is analyzed by means of Molecular Mechanics. It is shown that the most probable mechanism of SiOCH modification in He plasma is removal of hydrogen atoms from CH_3 groups. The change of Si–O–Si bond angles depends on the amount of the formed $–CH_2*$ (CH_x) groups. During the followed exposure in NH_3 plasma, NH_2* radicals bind CH_x groups with Si forming a –CH– Si–O–Si–O–Si–O–Si– chain. The end of this chain gets bound to its beginning through NH_2. This process is the reason of pore sealing.

INTRODUCTION

Porous SiOCH low-k films with carbon containing hydrophobic groups are the most favored class of materials for advanced interconnect technology. Although the matrix of these materials has properties similar to SiO_2, their chemical stability and reactivity strongly depend on porosity, pore size and their interconnectivity. The use of porous materials brings challenges related to the structural properties such as percolation phenomena. In addition to changes in mechanical properties (Young's modulus), porous materials exhibit high chemical activity, which brings complications to their application and technological processing.

The exposure of these films to a plasma leads to the loss of hydrophobic groups and to the densification of their silica backbone. Both effects cause an unwanted increase in the dielectric constant, as well as an increase in the leakage current. The extent of this damage depends on the plasma conditions such as chemistry and power and on the porosity of the film. On the other hand, treatment in certain plasmas [1, 2] may cause pore sealing, which results in a decrease in the chemical activity of these layers. Changing an inert gas and excluding the ion component in treating the surface the authors demonstrated that the film reactivity is affected by the UV radiation of the plasma. For instance, it was shown in [3, 4] that the treatment of SiO_2 films in He plasma caused an increase in the rate of etching these layers in 1% HF solution. Another observation is that sequent exposure of SiOCH low-k film in He and NH_3 plasma results in complete sealing and passivation of the film surface [1] .

The effect of porosity on chemical activity can be considered in two aspects: first, due to the developed surface, with the reaction proceeding not at the boundary but over the whole volume: we will call this effect macrostructural; second, due to changes in the electron structure of surface atoms, which leads to changes in the chemical properties of surface atoms: to be called microstructural effect. It is the investigation into the microstructural effect that will allow us to understand how we can change the properties of the surface atoms and their reactivity. The general idea of the changes in the electron structure under the action of an adsorbed molecule or atom was considered in [5]. The application of such an approach to sensor problem was described in [6]. The use of the idea of the transition adsorption complex proposed in [7]

allowed describing adsorption-stimulated surface reconstruction. A theoretical investigation of the dependence of chemical properties of molecules on the molecular structure can be useful because it may result in a substantial decrease in the time necessary for the search for necessary surface groups imparting the required surface properties. Theoretical considerations are also useful in view of the difficulties in the experimental analysis, since the surface groups concentration may be too small to be detected with the help of direct spectroscopic methods. In this situation, modeling may become the basic method to predict the characteristics of thus treated surfaces.

In the present work we consider low-k dielectrics based on silicon dioxide. It is known that the lability of Si–O–Si bonds is the main reason of differences in the adsorption properties of SiO_2 modified with different functional groups. For instance, an interconnection between the reactivity and Si-O-Si bond angle was described in [8]. As the second step of our recent work [1], we are making an attempt to explain with the help of modeling why the SiOCH low-k films change their chemical properties during the exposure in He and NH_3 plasmas.

The experimental data under consideration are those reported in [1] demonstrating how the layer characteristics change under treatment with different kinds of plasma. PECVD carbon-doped SiO_2 low-k films were deposited and UV cured. According to results obtained by ellipsometric porosimetry [9], the final porosity of the films was close to 25% and pore diameter was 2 nm. It was shown that their chemical behavior can change due to differences in Si-O-Si bond mobility, which determines the structure of SiO_2-based films. The IR spectra of the films show that they have different structures, namely, different Si-O-Si angles; an increase in the average angle value causes an increase in the intensity of the band at 1070–1150 cm^{-1}. Film reactivity is determined by the electronic structure and thus by bond geometry.

MODELING

Modeling is being increasingly frequently used for theoretical description of the properties of solids, including low-k dielectrics. For instance, the authors of [10] presented a theoretical investigation of the mechanical and dielectric properties of SiOCH films. In some cases, quantum-chemical and semiempirical methods can well predict or confirm the structure of these layers [11, 12]. The approach proposed in [7] involving calculations of an adsorption complex allows one to obtain additional data on the reactivity of these layers. The main idea of the proposed approach is that a reaction is considered through the formation of a definite intermediate state. The structure of this intermediate state referred to as an adsorption complex (AC) is calculated. This state is searched on the basis of the minimum energy; calculation results allow us to conclude whether such an adsorption complex exists and what are the directions of its further transformations.

Modeling was carried out by means of molecular mechanics MM2. A structure described below was used in modeling. The structure was optimized to the minimum of total energy, and changes in Si–O–Si bond angles were monitored; a distribution over the values of this angle was plotted. In order to do this, the range 135-153 ^{o} was divided into 10 intervals. Total number of Si–O–Si bond angles in the structure under calculation was 58. Thus obtained distribution is directly connected with the frequency of Si–O–Si bond vibrations in the IR spectrum. In other words, we modeled the IR spectrum depending on $d\pi$-$p\pi$ bonding. The experimentally determined vibration frequencies of Si–O bond [1] depending on Si–O–Si bond angle are shown in Table 1.

Table 1

Si–O–Si angle, deg	<140	144	155
frequency, cm^{-1}	1000	1070	1150

Molecular structure. The structure formed by the rings composed of –Si–O–Si–O atoms was used in modeling. Each ring contained 6 silicon atoms. These rings formed a structure shaped as a cylinder with the inner diameter corresponding to the pore size. The number of rings comprising the structure was chosen so that a pore 1 nm in radius could be obtained. The free bonds of the surface silicon atoms were considered to be filled with hydrogen atoms; a part of H atoms was substituted by methyl groups. Their amount corresponded to the method by which real films were prepared. The fraction of methyl groups was 20 – 25% of the number of silicon atoms. This amount corresponds to the films with the porosity about 25 % and pore radius 1 nm [12]. The structure is shown in Fig. 1.

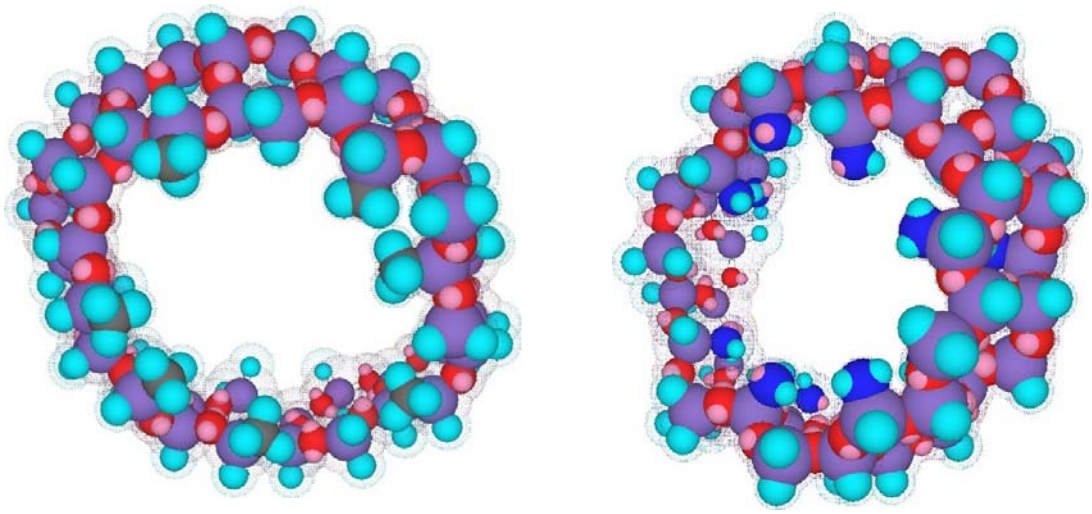

Fig. 1. Initial SiOCH structure (a) used for calculations, and the structure after treatment with ammonia plasma.

He plasma. The effect of He plasma on silicon dioxide was considered mainly as the interaction with CH_3 group because this group is the most available one from the viewpoint of energy and stoichiometry. It was assumed in calculations that a rupture of H atom or CH_3 group as a whole occurs. Calculation was carried out through the adsorption complex. This approach allowed us to determine the most probable reaction route.

It is shown in Fig. 2a-b how the calculated distribution of Si–O–Si bond angles changes depending on the amount of the introduced CH_2* (CH_x) groups. One can see in this distribution that the removal of hydrogen atoms results in an increase in the number of bonds characterized by the angle 144-146 ^{o}. Considering this surface treated in ammonia plasma one may assume that NH_2* interacts with a CH_2* group forming a Si – CH_2 – NH_2 chain. After the plasma is switched off, an unshared electron pair at the nitrogen atom forms a bond, due to Van der Waals forces, with a silicon atom inside the pore. The probability of the formation of such a bond in a pore is higher than at an open surface. It is most probable that the following reaction occurs: NH2*

binds CHx groups with Si, forming a chain looking like –CH– Si–O–Si–O–Si–O–Si–; the end of this chain gets bound to its beginning through NH_2. Changes in the distributuion of Si–O–Si angles in this situation are shown in Fig. 2-c. In order to explain the IR spectrum observed after treatment in the ammonia plasma without preliminary treatment in helium, we calculated several reasonable reaction models. The changes observed in experiments are best described with the following model: rupture of CH_3 groups, formation of Si–NH_2 and Si–CH_2–NH_2 bonds. Changes in Si–O–Si angle distribution during the interaction with ammonia are shown in Fig. 3. One can clearly see here that the most probable angle value is about 144-146^o. It should be noted that the number of angles equal to 142 ^{o} and smaller has decreased.

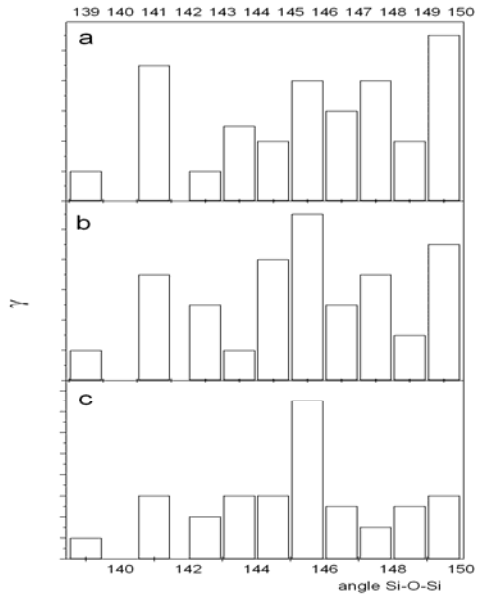

Fig. 2. Calculated distribution of Si–O–Si angles: a) initial structure (see Fig. 1a), b) formation of CH* groups, c) interaction with NH_2* after treatment in He plasma.

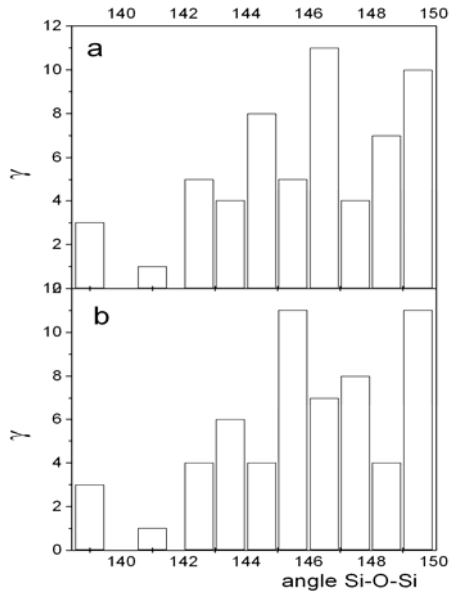

Fig. 3. Distribution of Si–O–Si angles: a) substitution of CH_3 for NH_2 groups, b) formation of CH_2–NH_2 bonds.

DISCUSSION

He plasma*:* since no increase in the intensity of the band at 1000 cm^{-1} is observed in experiments, one should not be sure that the process occurring in He plasma may be described mainly as the rupture of oxygen atom and its removal from the silicon atom with the formation of a dangling bond. Quire contrary, the observed decrease in the frequency of CH_3 group vibrations is connected either with the rupture of hydrogen or with changes in the dπ-pπ overlapping during the adsorption at the silicon atom, which increases the rigidity of the Si–O–Si bond. In turn, this causes weakening of the bond holding CH_3 group, which correspondingly results in a decrease in the frequency of CH_3 vibrations. A fact evidencing in favour of overlapping is that the intensity of the band at 1070 cm^{-1} and higher increases, which confirms an increase in the Si-O-Si angle. So, the IR spectra show that the treatment in He causes a decrease in the intensity of the band at 1000 cm^{-1} and an increase in the intensities of the bands within the range 1070-1150 cm^{-1}. These changes are due to the CH_3 groups. It is these groups that are able

to render (give) the electron density: a removal of a proton causes an increase in the Si-O bond order, that is, an active center is formed at the carbon atom: for example, CH_2* or CH_2^-. In both cases, the electron density shifts from the CH_x group ensuring an effective negative charge δ^- at Si atom. This causes changes in the geometry, namely an increase in the Si-O-Si bond angle. This model is in good agreement with our calculations. One can see in Fig. 2 a, b that, indeed, if we assume that a rupture of a proton from the CH_3 group occurs in He plasma, this results in a shift of the distribution toward larger angles. Subsequent treatment of the film in NH_3 plasma, after He, promotes cross-linking over these CH_x* groups, as well as Si atoms; NH_x* may serve as a bridge. It is clear that pore size decreases, or the pores get sealed, because the reaction proceeds at the very pore entrance. Because of this, if porosity is measured on the basis of the refractive index, one would not see any essential changes. It should also be noted that the number of built-in NH_2 groups may be small, since building-in occurs only on the surface; this may be the reason why these groups do not manifest themselves in the IR spectra. Modeling carried out by us shows that the angle distribution should not strongly differ from the initial state. It should be stressed that the angle distribution became more uniform, with the prevalence of one angle value (Fig. 2c). This also agrees with the IR spectrum in which we actually observe a small narrowing of the bands.

In the case of treatment with NH3 (without preliminary treatment in He), there are no active CH_x centers; the interaction proceeds mainly due to the formation of a bond between NH_x* and Si atom. The Si-O-Si angle increases, which causes an increase in the frequencies to 1070 and to 1150 cm^{-1}. The amount of adsorbed molecules can be estimated on the basis of the intensities of these bands. The band related to CH_3 group shifts to smaller frequencies, which is also an evidence of a strong increase in π-bonding in the Si-O-Si system. Since an increase in π-bonding causes an increase in Si-O-Si angle, a pore 1 nm in radius can increase by 0.4-0.5 Å (that is, by about 2 %), which is observed experimentally. The experimental data are in good agreement with modeling results. For instance, one can clearly see in the distributions shown in Fig. 3 a,b that the amount of bonds with 146-148 ^{o} angle increases; the angles smaller than 142 ^{o} disappear almost completely. Such a behavior is characteristic both of the case of the replacement of CH_x groups with NH_2 (Fig. 3a) and of the case of the addition of NH_2 groups at the silicon atoms (Fig.3b).

Note. Rupture of Si-O bonds in the volume, induced by the VUV radiation of He plasma, cannot result in a noticeable removal of the fragments formed; a most probable process may be recombination followed by redistribution of the excess energy over the lattice. It may be assumed that this process would not have any direct effect on changes in porosity. Because of this, here we do not consider the effect of VUV irradiation on the rupture of stronger bonds like Si-O-Si; however, we do not exclude this process. It should also be noted that an additional appearing dπ-pπ overlapping strengthens bonding between silicon and oxygen, which leads to an increase in the stability of this bond and a decrease in its reactivity.

CONCLUSIONS

Plasma modification of porous SiOCH films is analyzed by means of Molecular Mechanics. It is shown that the most probable mechanism of the modification in He plasma is formation of CH_x groups by removal of hydrogen atoms from CH_3 groups. This increases the number of Si–O–Si groups having bond angles in the range of 144-146 ^{o}. Subsequent exposure in NH_3 plasma forms –CH– Si–O–Si–O–Si–O–Si– chains where the end of the chain gets bound to its beginning

through NH_2. This process is the reason of pore sealing.

The results of modeling are in a good agreement with FTIR spectra presented in paper [1]. Additional support was obtained for different types of low-*k* material (Figure 4). One can see that the absorbance of Si-CH_3 groups is decreased after all plasma treatments. Additional NH_3 treatment shifts Si-O-Si frequency to higher wavenumbers. In the case of treatment in NH_3-based plasma, it is possible to incorporate the OSi-N bonds. The energy of those bonds is within the range of 874-1042 cm^{-1} [13]. Furthermore, they might be overlapped with Si-O-Si asymmetric stretching vibrations giving rise to Si-O-Si network peak (~144º) as shown in Fig 4. Those observations are in agreement with the results of modeling. A more complex situation is with the pure He and He + NH_3 plasma treatments. We clearly see incorporation of Si-O-Si with bond angle lower than 144 ^{o} for both He and He+NH_3 plasma, which demonstrates the possibility of breakage of Si-O bonds.

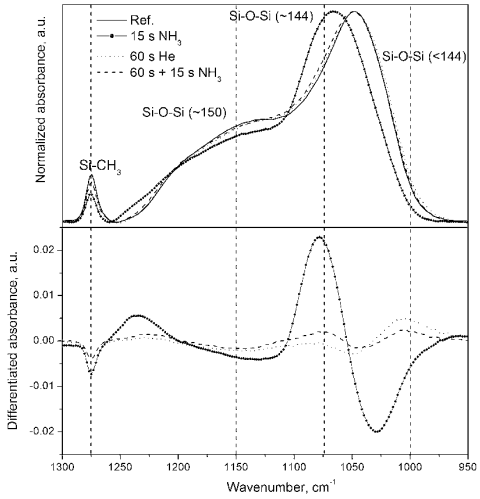

Fig. 4 Conventional (top) and differential (bottom) FTIR spectra of as deposited and plasma treated low-*k*.

References.

1. A. M. Urbanowicz et al. *Electrochem. Sol.-St. Lett.*, 10 /10, G76 (2007) .
2. H.G. Peng et al.. *J. Electrochem. Soc.*, 154(4) G85 (2007).
3. T. Tatsumi, S. Fukuda, S. Kadomura. *Jpn. J. Appl. Phys*. 32, 6114 (1993).
4. T. Tatsumi, S. Fukuda, S. Kadomura. *Jpn. J. Appl. Phys*. 33, 2175 (1994)
5. Wolkenstein T., *Electronic Processes on Semiconductor Surfaces during Chemisorption*, (Consultants, 1991) pp. 35-182.
6. Rothschild A., Komem. *Sensors and Actuators*. B93. 362 (2003).
7. F.N. Dultsev, L.L. Sveshnikova. *Sensors & Actuators*, B120, 434 (2007).
8. F. Dultsev. *J. Struct. Chem*. 48/2, 236 (2007).
9. M. R. Baklanov et al. *J. Vac. Sci. Technol. B 18*, 1385 (2000).
10. N. Tajimaa et al.. *Appl. Phys. Lett.*, 061907 (2006)
11. K. Zagorodniy, H. Hermann, and M. Taut. *Phys. Rev.,* B 75, 245430 (2007)
12. A.S. Zyubin et al.. *J. Chem. Phys.,* 116/1, 281-294. (2002).
13 J. Olivares-Roza, O. Sanchez, and J. M. Albella, J. Vac. Sci. Technol. A**16**, 2757 (1998)